Synopsis of the First National Lab and University Alliance Workshop on Ultrafast Electron Microscopies

The recent explosion of research in pump-probe studies of the picosecond time-dependence of chemical reactions has been based largely on laser induced and laser interrogation techniques, or on laser induced and synchrotron radiation interrogation techniques. Applications include study of the time evolution of phase transitions in condensed matter and of excited (partially unfolded) proteins. The observation of intermediate metastable states is of particular interest in gaining insight to reaction pathways. However, much less attention has been given to approaches based on laser induced and electron interrogation methods, despite the fact that electron sources are brighter and their interactions with matter stronger. Use of electrons as probes has great potential for study of complex transient events, not only because of the possible high temporal resolution, but also the potential for high spatial resolution imaging.

UED and DTEM will provide quantitative characterization and understanding of materials structure and its evolution over atomic to micron length scales and ps to μs time scales.

Introduction

The First National Lab and University Alliance Workshop on Ultrafast Electron Microscopies was held on April 16–17, 2004 at the Pleasanton Hilton at the Club in Pleasanton, California in response to growing interest in use of electrons as an ultrafast probe for chemistry, biology, and materials science. The workshop was organized by Lawrence Livermore, Los Alamos, and Sandia national laboratories. Major support came from the National Nuclear Security Administration, and the workshop was sponsored by E.A. Fischione Instruments, Inc., Gatan, Inc., FEI Company, JEOL, USA, Inc., and LEO USA, Inc.

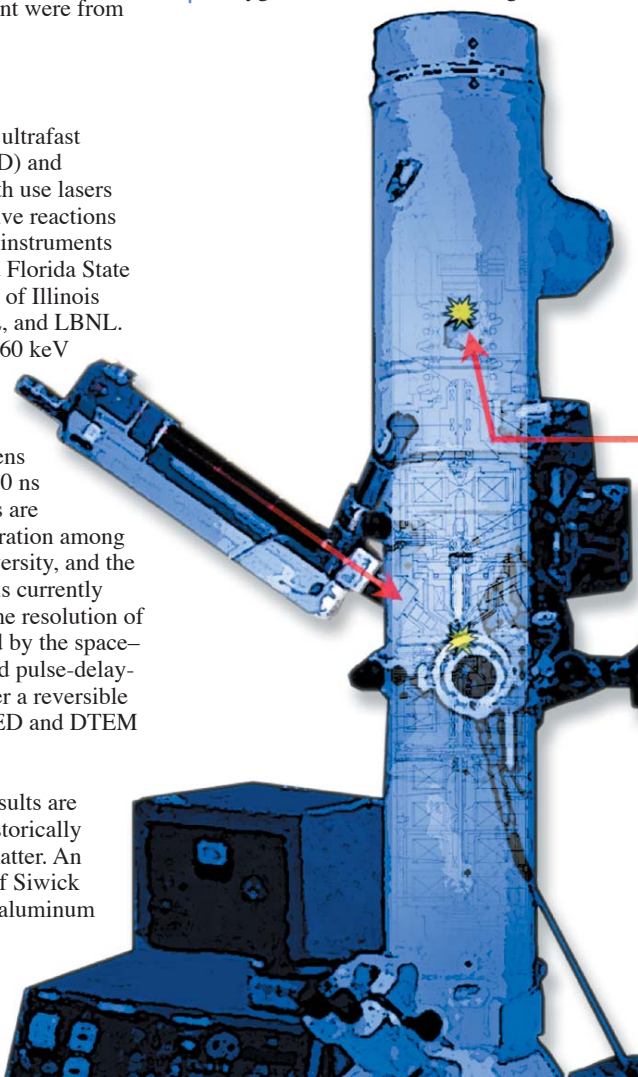
The workshop was attended by 51 participants from universities, national laboratories, industry, and government. (Figure 1). Twenty-five percent of the participants were invited and 12 percent were from countries other than the United States.

Science

UED and DTEM. Two methods employing electrons as ultrafast probes were discussed: ultrafast electron diffraction (UED) and dynamic transmission electron microscopy (DTEM). Both use lasers to produce electron pulses (by photo emission) and to drive reactions at the specimen. UED currently dominates the field with instruments at Caltech, Brown University, University of Toronto, and Florida State University. New instruments are proposed for University of Illinois at Urbana Champaign, Michigan State University, LLNL, and LBNL. UED instruments typically have electron energies of 30–60 keV and time resolutions down to 500 fs using thousands of electrons per pulse to form time-resolved electron diffraction patterns. DTEM exists only at the Technische Universität Berlin and uses 100-keV electrons in a Siemens ELMISKOP 1A. The DTEM has time resolution of ~3–10 ns using ~10^8 electrons to produce electron images. DTEMs are planned at LLNL, University of Michigan, and a collaboration among the University of California at Davis, Arizona State University, and the University of Illinois at Chicago. The LLNL instrument is currently under construction and is planned to have an imaging time resolution of 1 ns with a goal of 30 ps. Because of limitations imposed by the space–charge effect, most UED systems are limited to integrated pulse-delay-probe multishot experiments. This requires study of either a reversible process or new samples for each shot. A goal for both UED and DTEM is single-shot experiments.

MATERIALS SCIENCE. The first materials science results are just now becoming available as laboratories that have historically focused on chemistry turn their attention to condensed matter. An often-quoted result is shown in Figure 2 from the work of Siwick et al.[1] In this work, the laser-induced melting kinetics of aluminum were determined using UED. Aluminum was found to melt within 1.5 ps of the time that it is irradiated with the laser. The authors claim this to be the first fully resolved solid-to-liquid phase transformation. In the future, UED and DTEM will advance our understanding of mechanisms of a variety of phase transformations including transitions from crystalline to non-crystalline phase, crystalline to crystalline, crystalline to liquid, crystalline to plasma, and liquid to solid. UED and DTEM will provide quantitative characterization and understanding of materials structure and its evolution over atomic to micron length scales and ps to μs time scales.

BIOLOGY. UED and DTEM have the potential for revealing important transition pathways in biology, such as the release of oxygen from hemoglobin.[2] When oxygen is released, a breathing



UCRL-ABS-203750

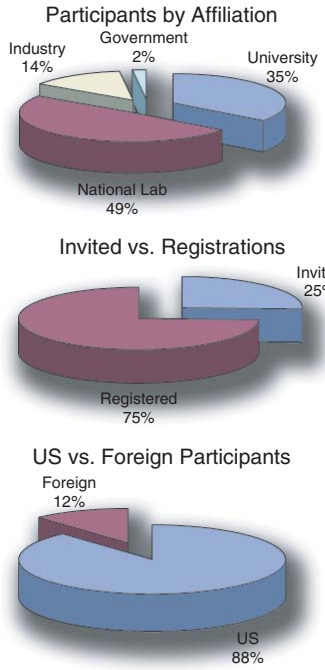


Figure 1. Breakdown of workshop participants.

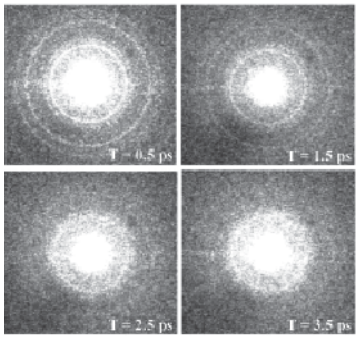


Figure 2.UED observation of the ultra-fast melting of aluminum.[1]

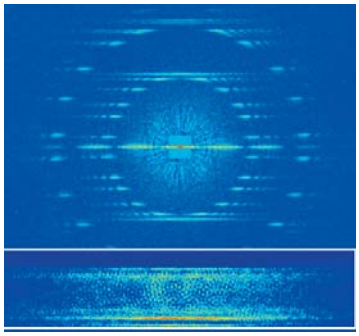


Figure 3. Diffraction pattern (at top) and reconstruction (at bottom) of a double-walled carbon nanotube.[3]

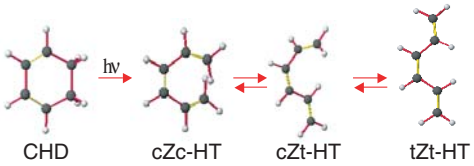


Figure 4. Important reaction pathway revealed by UED.[4]

mode is induced within the molecule. This quantum fluctuation results in changes to the long range structure of the molecule and to the binding efficiency of the oxygen. UED has the potential for unlocking the secrets of these kinds of conformation changes that lie at the heart of protein function.

The potential also exists for diffractive imaging using UED and the resulting three-dimensional reconstructions of large structures at high resolution. An example of the reconstruction of a double-walled carbon nanotube made with conventional electron diffraction is shown in Figure 3.[3] Ultrafast methods may give access to the structure of radiation sensitive materials if structural data from the material can be encoded in the electron or x-ray pulse before the structure is destroyed. Electrons are expected to play a role in this new area because brightnesses and interaction cross sections are much larger than those of typical x-ray measurements and the amount of damage induced per elastically scattering event is lower for electrons than for photons.

Diffractive imaging can also be used to determine the structure of aligned small molecules. In this case, ultrafast is used to obtain time resolution, not to overcome damage. Another area for the application of aligned molecules is time-resolved electron diffractive imaging of membrane crystals (or other 2D protein crystals).

CHEMISTRY. There are many photostimulated reactions that proceed at rates in the fs or ps time scale. Almost all molecules that can be taken to the gas phase have been studied using static electron diffraction. Time-resolved electron diffraction is now being applied to study chemical reactions in real time. A classic example is the electrocyclic ring-opening reaction of 1,3-cyclohexadiene (important in the production of vitamin D) illustrated in Figure 4. Using UED, Dudek et al. identified the likely transition pathway for the opening of this molecule.[4] UED is being applied to target molecules in the gas phase, as crystals, on surfaces, and in the liquid state.

Technology

ELECTRON SOURCES. Current-generation UED and DTEM instruments are all based on laser-driven photocathodes and DC accelerating voltages. The time resolution of these systems is fundamentally limited by the space–charge effect. It is possible to overcome this limitation by increasing the accelerating voltage to a point where relativistic effects overwhelm the space–charge effect. These sources can achieve 10^8–10^9 electrons in a 2-ps pulse in MeV beams.[5] Further improvements in time resolution may be obtainable using laser wakefield acceleration, where electrons are produced by laser irradiation directly at MeV energies.

ELECTRON PULSE COMPRESSION. Ultimately, in the absence of highly relativistic electrons, pulse compression will be required for the desired single-shot experiments using both diffraction and imaging. Technologies for such pulse compression exist and are enabled by the naturally occurring linear chirp of electron energies in UED or DTEM.[6]

ELECTRON DETECTORS. The majority of UED and DTEM systems in existence use microchannel plate electron detectors. Advances in design should enable use of CCD detectors with a scintillating medium, or direct detection of the electrons in a radiation-hardened solid-state device. These monolithic detectors appear to be excellent candidates for electron microscopy offering complex functionality, excellent position resolution, and high sensitivity to electrons.

COMPARISON WITH X-RAYS. Several presenters made detailed comparisons between ultrafast electron methods and ultrafast x-ray methods. The methods are clearly complementary with electrons holding the yet unrealized potential for high spatial resolution, high time-resolution imaging.

Conclusions

The use of electrons as an ultrafast probe provides direct investigation of transient atomic positions via diffraction and defect structures via imaging, which opens up new areas of science and technology for investigation. The technology requires a multidisciplinary team with specialists in physics, chemistry, biology, and materials science collaborating to solve fundamental problems. The goal is the "molecular, chemical, or material movie" where complex transient phenomena are resolved in time, allowing the discovery of reaction pathways. Resolving the molecular state in a time-resolved way for transitions would give us invaluable clues for how to take advantage of observed dynamics.

References

1. B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, *Science,* **302**, 1382-1385 (2003).
2. R. J. D. Miller, in "UED in Materials Science and Biology," presented at the *First National Laboratory and University Alliance Workshop on Ultrafast Electron Microscopies*, Pleasanton, CA, 2004.
3. J. M. Zuo, I. Vartanyants, M. Gao, R. Zhang, and L. A. Nagahara, *Science,* **300**, 1419-1421 (2003).
4. R. C. Dudek and P. M. Weber, *Journal of Physical Chemistry A*, **105**, 4167-4171 (2001).
5. J. F. Schmerge, P. R. Bolton, J. E. Clendenin, F. J. Decker, D. H. Dowell, S. M. Gierman, C. G. Limborg, and B. F. Murphy, *Nuclear Instruments & Methods in Physics Research*, "Section A-Accelerators, Spectrometers, Detectors, and Associated Equipment," **483**, 301-304 (2002).
6. B. J. Siwick, J. R. Dwyer, R. E. Jordan, and R. J. D. Miller, *Journal of Applied Physics*, **92**, 1643-1648 (2002).

FOR MORE INFORMATION CONTACT

Wayne King 925.423.6547 weking@llnl.gov

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.